The Carbon-Rare Earth Systems

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Equilibrium Diagrams

Phase diagrams, either partial or nearly complete, have been reported for only three RE-C systems. [59Spe] examined the La-C system extensively and proposed a phase diagram that is the prototype for systems of C with the light rare earths (RE = La, Ce, Pr, and Nd). [64Ste] reported a phase diagram for the Ce-C system, but the entire liquidus and the peritectic and eutectic horizontals were presented as dashed lines because their diagram was based on only a few thermal analysis data points and metallographic observations. A phase diagram for the Y-C system was proposed by [68Car] and refined by [71Sto]. Because Y behaves much like Dy and Ho, the Y-C phase diagram may be regarded as the best prototype available for the heavy-lanthanide systems with C. However, it was shown by [67Kri] that LuC_2 has a different stable room temperature structure from the other heavy lanthanide dicarbides, although the stable high-temperature form for LuC_2 was reported to be the same as that of REC_2 where RE = La, Ce, Eu, or Tb. Because of this behavior, the Lu-C system may not precisely follow this prototype. Also, the structure and composition of the intermediate phases as a function of atomic number change at about Ho. [58Spe] observed that the rare-earth sesquicarbides from La to Ho (Pm and Eu not examined) have bcc structure of the Pu_2C_3 type, whereas sesquicarbides of Ho, Er, Tm, and Lu are isostructural with Y_2C_3. [71Bau] subsequently found that these "sesquicarbides" of Y and the heavier lanthanides actually have the formula $RE_{15}C_{19}$ and tetragonal structure. This further limits the number of heavy lanthanide-carbon systems for which the Y-C system may be a prototype.

In addition to the phase diagram studies, several investigators have reported melting temperatures for RE_2C_3 [69Pad1, 70Yup, 71Kos], $\alpha \rightleftarrows \beta$ transformation temperatures for REC_2 [67Bow, 67Kri, 67Win, 69Pad2, 73Mcc, 74Ada, 76Ada, 76Loe, 78Ada, 81Mcc], temperatures for the REC_2-C eutectic [67Kri, 69Gre, 67Win], and melting temperatures for REC_2 [64Kos, 65Mak, 66Pad, 69Gre, 70Yup, 71Kos, 81Mcc]. Not all of those published data are in agreement, but where there are sufficient reports, the data may be examined by systematics [83Gsc] and the more logical values selected.

Mischmetal-Carbon Diagram. Figure 1 shows the hypothetical C-ideal mischmetal (MM) system. This diagram was drawn using methods described by [82Pal] with the incomplete data that are available for the several RE-C systems involved. [82Pal] assumed that the ideal MM contains 27 at.% La, 48 at.% Ce, 5 at.% Pr, 16 at.% Nd, and 4 at.% other RE that behave as 2 at.% Gd and 2 at.% Y. Of the six RE-C systems that make up this ideal MM, only the La-C and the Y-C systems are known in enough detail to allow a nearly complete phase diagram to be drawn. However, some melting point, transformation,

Fig. 1 Hypothetical Ideal MM-C Phase Diagram

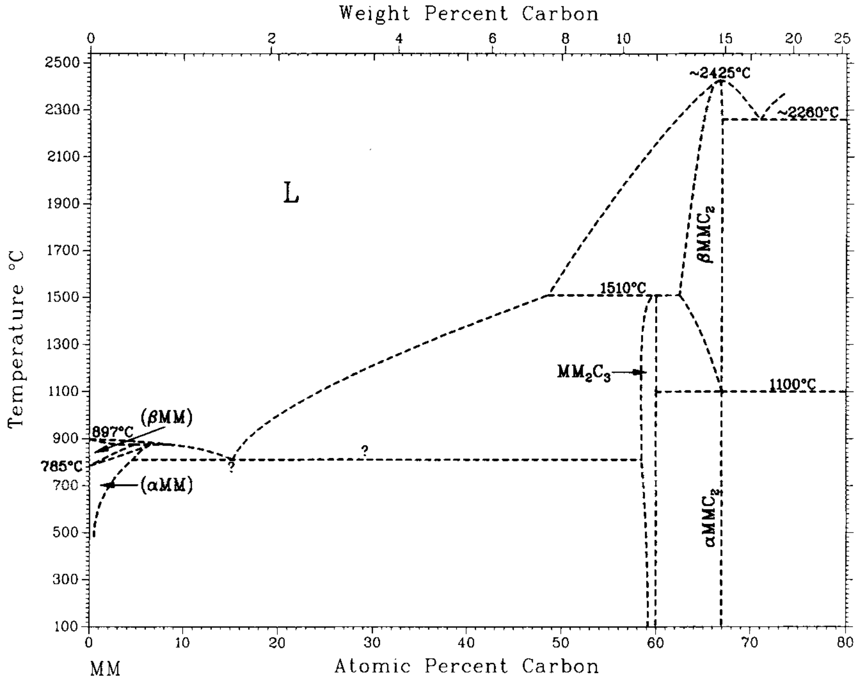

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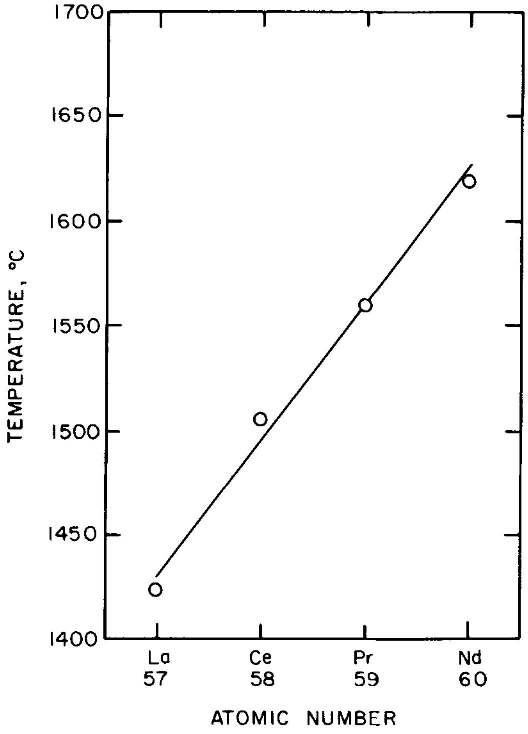
Table 1 Decomposition Temperature of RE_2C_3 Compounds

Compound	Temperature, °C	Standard deviation	Reference
La_2C_3	1423	8	[59Spe, 69Padl, 70Yup, 71Kos]
Ce_2C_3	1505	48	[69Padl, 70Yup, 71Kos, 69And]
Pr_2C_3	1560	...	[71Kos]
Nd_2C_3	1620	50	[69Padl, 70Yup]
Y_2C_3	1645	5	[68Car, 71Sto]

Data not used: A duplicate value for the melting point of La_2C_3, 1430 ± 20 °C reported by both [69Padl] and [70Yup], was used only once in calculating the average shown above. The duplicate value of 1530 ± 30 °C for Ce_2C_3 from the same sources was used once. These authors, as well as [71Kos], gave 1800 °C for $Y_{15}C_{19}$ (Y_2C_3), which is in poor agreement with values given by [68Car] and [71Sto] in well-documented phase diagram investigations. A partial phase diagram for the Ce-C system by [64Ste] showed an incongruent melting point for Ce_2C_3 at a temperature between 1800 and 1900 °C.

Fig. 2 Decomposition Temperatures of RE_2C_3 Compounds



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and eutectic point temperatures in the other four systems have been reported, and these data make it possible to draw an equilibrium diagram that we consider accurate regarding the phases encountered and fairly accurate on many of the important temperatures. Figure 1 is generally similar to the La-C equilibrium diagram; a complete Ce-C diagram would have been even more useful, because Ce makes up 48% of the ideal MM. In drawing the MM-C diagram, it was assumed that the Ce-C, Pr-C, and Nd-C systems are analogous to the La-C system, as stated by [59Spe]. It was also assumed that the sesquicarbide of each of these lanthanides decomposes peritectically at temperatures that increase systematically with atomic number. It is especially important that Ce, which often exhibits a variable valence, behaves as a trivalent metal and follows the lanthanide contraction; this may be the least likely of the assumptions made. We believe we made reasonable assumptions on some missing temperatures in the Gd-C system, but an error here is of less importance than in the light RE-C systems, because Gd and Y together make up only 4.0 at.% of the MM.

The high-MM side of the diagram is drawn much like the La-C diagram, but exact composition and temperature data are not known in this region for the MM-C compositions. The eutectic horizontal is placed above the $\alpha \rightleftarrows \beta$ transformation temperature and below the melting temperature of the ideal MM. Only the RE-RE_2C_3 eutectic composition where RE = La is known; consequently, there is no information to establish a systematic trend for this property.

A peritectic reaction is shown to occur at 1510 °C, where MM_2C_3 decomposes to the melt and βMMC_2. [58Spe] found that sesquicarbides of La, Pr, Nd, and Gd exhibit solid solubility; because Ce_2C_3 does not, and because Ce is 48 at.% of the ideal MM, the solid solubility region for MM_2C_3 was narrowed from that of the La-C phase diagram (see "The C-La (Carbon-Lanthanum) System," in this issue). However, not enough numerical data are available to show this lower solubility limit with any precision. This is also true of the liquidus line, except at the melting temperature for MMC_2, ~2425 °C. The amount of Y present in the MM, 2 at.%, is too small to introduce the tetragonal $Sc_{15}C_{19}$-type structure. MM_2C_3 would have the cubic Pu_2C_3-type structure observed with RE_2C_3 where RE = La, Ce, Pr, Nd, and Gd.

The other compound, the dicarbide MMC_2, exists in the tetragonal CaC_2-type structure below 1100 °C. At this temperature, αMMC_2 transforms to cubic CaF_2-type structure. [59Spe] found a region of solid solubility for LaC_2 that extended from about 1300 °C to the melting point. No similar information is available on the Ce-C, Pr-C, and Nd-C systems, except that [59Spe] stated that these systems are analogous to the La-C system. In Fig. 1, such a region is shown for βMMC_2, but there are only the LaC_2 data to suggest the lower solubility limit. The MMC_2-C eutectic composition is not known, because this composition was not given for any of the individual RE-C systems. A eutectic temperature of ~2260 °C was obtained by applying the method of [82Pal] to calculate MM properties from the reported data for the RE-C systems involved.

Decomposition Temperatures of RE_2C_3 Compounds. Data for the decomposition temperatures of RE_2C_3 compounds are scarce. [58Spe] reported that La_2C_3 decom-

Table 2 Tetragonal ⇄ Cubic Transformation Temperatures in REC_2 Compounds

Compound	Temperature, °C	Standard deviation	Reference
LaC_2	1060	35	[67Bow, 67Kri, 73Mcc, 74Ada, 76Ada, 76Loe, 78Ada]
CeC_2	1100	10	[67Kri, 73Mcc, 76Loe, 78Ada, 67Win]
PrC_2	1130	30	[67Kri, 76Loe, 67Win]
NdC_2	1150	20	[67Kri, 73Mcc, 74Ada, 76Ada, 76Loe, 81Mcc]
SmC_2	1170	20	[67Kri]
EuC_2	350	...	[82Sak]
GdC_2	1240	25	[67Kri, 73Mcc, 74Ada, 76Ada, 76Loe]
TbC_2	1288	4	[67Kri, 74Ada, 76Ada, 78Ada]
DyC_2	1290	30	[67Kri, 73Mcc, 74Ada, 76Ada, 76Loe]
HoC_2	1300	20	[67Kri, 73Mcc, 76Loe]
ErC_2	1310	25	[67Kri, 73Mcc, 74Ada, 76Ada, 76Loe]
TmC_2	1355	20	[67Kri]
LuC_2	1450	55	[67Kri, 73Mcc, 76Loe]
YC_2	1324	5	[67Kri, 76Ada, 68Car, 71Sto]

Note: The average values were rounded off to the nearest 10 °C, except for TbC_2 and YC_2. SmC_2, EuC_2, and TmC_2 values were reported by single investigators.

Date not used: [59Spe] reported 1800 ± 100 °C for the $\alpha \rightleftarrows \beta$ transition in LaC_2, a value much higher than any other temperature reported for this compound. The data of [69Pad2] for LaC_2 (950 ± 10 °C), CeC_2 (975 ± 25 °C), PrC_2 (980 ± 45 °C), NdC_2 (1005 ± 70 °C), SmC_2 (1070 ± 85 °C), GdC_2 (1100 ± 85 °C), TbC_2, DyC_2, and ErC_2 (each 1120 ± 80 °C), TmC_2 (1172 ± 65 °C), and YC_2 (1090 ± 80 °C) were not used because each value was considerably below the average for its set. Several papers reported identical values that were obviously based on the same investigations ([67Bow] and [67Kri] for LaC_2 and LuC_2, [78Ada] and [76Ada] for LaC_2, [74Ada], [76Ada], and [78Ada] for GdC_2); in each instance, the value in question was only used once in obtaining the mean temperature for the set. [64Chu] reported ~1500 °C for YC_2.

poses incongruently at 1415 ± 3 °C, and [64Ste] indicated peritectic decomposition for Ce_2C_3, without citing a definite temperature. [69Pad1] reported "melting points" for La, Ce, Nd, and Y sesquicarbides to be 1430 ± 20, 1530 ± 30, 1620 ± 30, and 1800 ± 30 °C, respectively, but did not specify congruent or incongruent melting. [70Yup] listed identical values, and because the authors also wrote [69Pad1], these two papers are regarded as a single source. [71Kos] reported the same melting temperature for Y_2C_3, slightly different values for La_2C_3 and Ce_2C_3, 1560 °C for Pr_2C_3, but none for Nd_2C_3. They also made no mention of the type of melting. [68Car] investigated the Y-C system and found a monophasic field containing 55 to 58 at.% C with a congruent solid state transformation at 1645 °C and 58 at.% C. [71Sto] reported that Y_2C_3 decomposes congruently when heated to 1652 °C. The average of these two decomposition temperatures for "Y_2C_3," 1648 °C, seems to be more reliable than the 1800 °C temperature reported by [69Pad1], [70Yup], and [71Kos].

The averaged values for the assessed decomposition temperatures for the sesquicarbides of La, Ce, Pr, and Nd are shown in Table 1. The Y data are included also, although [71Bau] showed this compound to have the formula $Y_{15}C_{19}$ instead of Y_2C_3, as it is often referred to in the literature. Figure 2 shows the averaged decomposition temperatures of the light lanthanide sesquicarbides plotted against the atomic number of the lanthanide. A good correlation between decomposition temperature and atomic number is seen in this plot.

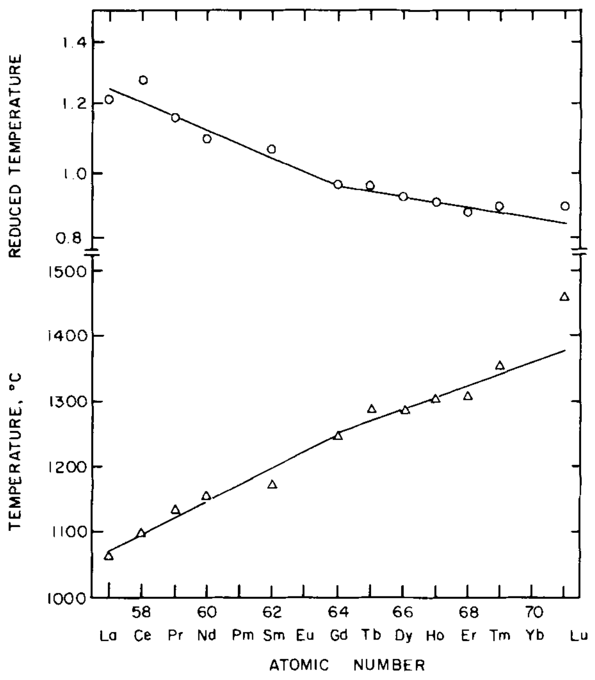
Solid-State Transformation Temperatures of REC_2. Fifteen papers were found that reported or repeated values for the transition temperature of this form in one or more of the RE-C systems. No values were found for the temperature of this transition in PmC_2, YbC_2, or ScC_2. In the Sc-C system, the dicarbide does not appear to exist. The Pm-C system has not been investigated and, although tetragonal lattice parameters have been reported for YbC_2, neither a transformation temperature nor a high-temperature form of YbC_2 has been reported.

[67Kri] investigated this transformation and also reported lattice spacings for several dicarbides, as well as melting temperatures of REC_2-C compounds and REC_2-C eutectic temperatures (to be discussed below). Raw materials were spectrographic grade C (graphite) in which B, Mg, and Na were the major impurities, each present in less than 50 ppm (wt.?). Impurities in their RE metal were in quantities less than 500 ppm. LaC_2 specimens were prepared by two methods: (1) arc melting the components on a water-cooled Cu hearth, using a graphite electrode under a Zr-gettered He atmosphere; and (2) induction heating in a sealed Ta crucible under a vacuum of ~10^{-3} Pa at the reaction temperature or under a partial pressure of purified He.

The transformation temperatures were determined using pressed plugs of mixtures of REC_2 with excess C. A sight hole 1.5 by 9.5 mm was drilled into the top of each cylinder for optical pyrometer measurements. The REC_2-C eutectic temperature was determined by a cooling curve method, wherein light from the sight hole was divided by a beam splitter, and one beam focused on a sensing diode that was connected to the *y* axis of an oscilloscope. Upon heating or cooling through the eutectic temperature or through the $\alpha \rightleftarrows \beta$ transformation temperature, a flat in the trace was observed. The traces were recorded by a Polaroid camera, and the actual temperature was determined from the other beam. The arc-melted dicarbides were analyzed for RE, total C, and free C, and after measurements had been completed, for RE and total C. Lattice parameters were also obtained from back-reflection lines, using a least-squares extrapolation method. High-temperature X-ray patterns for LaC_2, TbC_2, and LuC_2 were obtained using hot pressed cylinders in a vacuum of better than 10^{-2} Pa.

[76Loe] prepared samples of nine rare-earth dicarbides by arc melting the metals (purity >99.9%) and spectroscopically pure C rod in stoichiometric amounts under purified argon in an arc furnace. Transformation temperatures were investigated by the cooling curve technique,

Fig. 3 $\alpha \rightleftarrows \beta$ Transformation Temperatures and Reduced Transformation Temperatures of REC_2 Compounds



The anomalous value for LuC_2 is probably due to the fact that αLuC_2 has a structure different from other αREC_2 phases.
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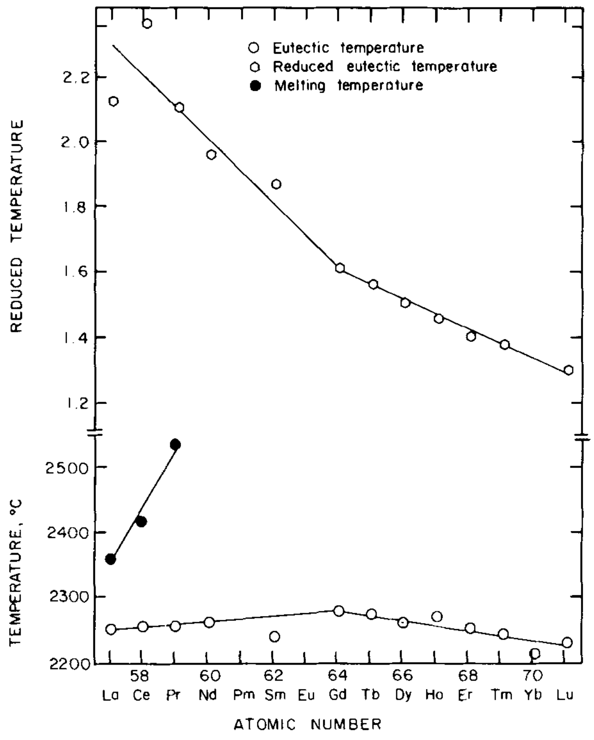
Fig. 4 REC_2-C Eutectic and REC_2 Melting Temperatures and Reduced Eutectic Temperatures



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with a solid-state pyrometer focused on the specimen and the output fed to a high-speed recorder. The temperature scale was calibrated using the freezing points and transition points of pure lanthanide metals. Most of their transformation temperatures were obtained from boules weighing less than 0.5 g that were quenched rapidly on the water-cooled Cu hearth of their arc furnace. [76Loe] reported $\alpha \rightleftarrows \beta$ transformation temperatures obtained on heating and on cooling in a differential thermal analysis (DTA) apparatus. Some hysteresis was shown to exist in the transformation, because the values obtained on heating were 7 to 15 degrees higher than those obtained on cooling. Values obtained in their DTA apparatus generally were higher than those obtained in the arc furnace, except for GdC_2, where the difference was reversed, and for HoC_2 and ErC_2, where the difference all but vanished. All three sets of values were used in our application of systematics.

One set of data not included was that reported by [69Pad2], who measured electrical resistivity, thermoemf, and thermal expansion as functions of temperature, reporting a set of temperatures at which the transformation appeared to begin in various dicarbides. Their values are lower than other reported transition temperatures for the corresponding dicarbides. Another value not used is that of [59Spe] for the $\alpha \rightleftarrows \beta$ transformation in LaC_2, which on the basis of electrical resistivity measurements they reported as occurring at ~1800 °C. [67Kri], who noted a difference of 740 °C between their value (1060 °C) and that of [59Spe], searched the higher temperature region, and concluded that [59Spe] had observed some other phenomenon.

The acceptable reported data were averaged for each individual dicarbide, and reduced temperatures based on these averages were calculated. These data are presented in Table 2 and plotted in Fig. 3. The plot shows the transformation temperatures of the individual dicarbides lying close to a straight line that connects the transformation temperatures of LaC_2 and GdC_2. Another straight line, from the GdC_2 transformation temperature running through the HoC_2 transformation temperature, roughly defines this value for the heavy lanthanide dicarbides. An exception is the temperature for the $\alpha \rightleftarrows \beta$ transformation of LuC_2, which is anomalously high. This is not unexpected, because αLuC_2 has a different stable form from the other αREC_2 compounds.

The fact that an $\alpha \rightleftarrows \beta$ transformation has been observed in most of the REC_2 compounds strongly suggests that the high-temperature form of REC_2 has the CaF_2, *C*1-type structure, as has been observed for βREC_2 where RE = La, Ce, Eu, Tb, and Lu.

REC_2-C Eutectic and REC_2 Melting Temperatures. [67Kri] reported temperatures for 14 of the REC_2-C eutectics, but there are few other data to confirm or contradict their findings. [59Spe] reported 2271 ± 15 °C for the LaC_2-C eutectic, and [67Kri] reported 2230 ± 20 °C. For

Table 3 Eutectic and Melting Temperatures of REC_2 Compounds

Compound	Temperature, °C	Standard deviation	Reference
REC_2-C eutectic temperatures (a)			
LaC_2	2250	30	[59Spe, 67Kri]
CeC_2	2260	20	[67Kri, 67Win, 68Fai]
PrC_2	2255	20	[67Kri]
NdC_2	2260	30	[65Mak, 66Pad, 68Fai, 70Yup, 71Kos, 81Mcc]
SmC_2	2240	30	[67Kri]
GdC_2	2280	30	[67Kri, 70Yup, 71Kos]
TbC_2	2275	20	[67Kri]
DyC_2	2260	25	[67Kri, 70Yup, 71Kos]
HoC_2	2270	20	[67Kri]
ErC_2	2260	25	[67Kri, 70Yup, 71Kos]
TmC_2	2245	35	[67Kri]
YbC_2	2215	40	[67Kri]
LuC_2	2230	20	[67Kri]
YC_2	2290	20	[64Kos, 67Kri, 68Car, 71Sto]
REC_2 melting temperatures (b)			
LaC_2	2360	25	[59Spe, 65Mak, 67Kri, 71Kos]
CeC_2	2420	180	[64Kos, 65Mak, 66Pad, 70Yup, 71Kos]
PrC_2	2540	100	[64Kos]
YC_2	2415	25	[68Car, 71Sto]

(a) The average values were rounded off to the nearest 10 °C. For those compounds for which only one measurement was made, the values were left unchanged as reported by the investigators. **(b)** All values were rounded off to the nearest 10 °C except for YC_2, where both investigators gave the same melting point.

Data not used: Several reports contained eutectic or melting point temperatures that were attributed to earlier investigators such as[69Gre], who cited [67Kri] on eutectic temperatures of LaC_2-C, LuC_2-C, and YC_2-C. Several Russian publications [65Mak, 66Pad, 70Yup, 71Kos] gave the same value for some melting-point and/or eutectic data, and it is not clear that these are independent determinations; where the coauthors are the same people and the values are identical, these data have been treated as one source. Certain data reported as melting-point temperatures for REC_2 compounds have been considered by the reviewers to more likely be REC_2-C eutectic data and have been treated as such when compatible with other data that were known to be eutectic data. This category includes the melting-point data of [68Fai] for CeC_2 (2250 ± 20 °C) and NdC_2 (2290 ± 10 °C), as well as melting-point data from [65Mak] for NdC_2 (2207 °C), from [66Pad] for NdC_2 (2260 °C), from [70Yup] for NdC_2 (2260 ± 60 °C), for GdC_2 (2260 ± 60 °C), for DyC_2 (2250 ± 60 °C) and for ErC_2 (2280 ± 60 °C), from [71Kos] for NdC_2 (2207 °C), for GdC_2 (2265 °C), for DyC_2 (2245 °C), and for ErC_2 (2230 °C), and from [64Kos] for YC_2 (2300 ± 50 °C). The "melting-point" temperatures for PrC_2 listed by [65Mak], [66Pad], [70Yup], and [71Kos] ranged from 2147 to 2160 °C, about 100 °C below the eutectic temperature, 2255 ± 60 °C reported by [67Kri] for PrC_2-C. These low "melting temperatures" were therefore discarded. For a similar reason, the melting point of TbC_2 reported by [70Yup] (2100 ± 60 °C) and the melting point for TmC_2 reported by [71Kos] (2180 °C) were not used. These low values would be expected if the alloys studied were deficient in C, because the liquidus drops off sharply on the metal-rich side of REC_2, as shown in the well-established La-C and Y-C systems.

the Ce-C system, [67Win] reported 2270 ± 20 °C for this eutectic, compared with 2245 ± 20 °C from [67Kri]. For the YC_2-C eutectic, [67Kri] reported 2275 ± 25 °C, and their data were quoted by [69Gre], whereas [68Car] and [71Sto] gave 2305 ± 25 °C for the eutectic between YC_2 and C.

Several investigators have reported melting temperatures for REC_2 compounds that are lower than the eutectic temperature reported by [67Kri] for the corresponding REC_2-C eutectic. The melting points of LaC_2 and of YC_2 were established by [59Spe] and [68Car] as 2356 ± 25 and 2416 ± 25 °C, respectively. [64Kos] listed 2438, 2540, and 2535 °C (each with error limits of ±100) as the melting temperatures of LaC_2, CeC_2, and PrC_2, respectively. Considering the error limits, their value for LaC_2 is in agreement with that of [59Spe], and disregarding CeC_2 because Ce has a variable valence and often does not obey a systematic order, the trend appears to be higher melting temperatures with increasing atomic number of the light RE metal in the dicarbide. This trend would be expected to show a maximum melting temperature at GdC_2, then decreasing melting temperatures as the atomic number of the RE member of the dicarbide increases. The value for YC_2 would lie near or between the congruent melting temperatures of DyC_2 and HoC_2. These considerations suggest strongly that those reported melting points which lie between 2150 and 2290 °C are eutectic temperatures, and cannot be regarded as congruent melting temperatures. Some of the low temperatures reported as melting points of PrC_2 were discarded as being unreasonably low even for the PrC_2-C eutectic, but other reported melting temperatures for several other REC_2 phases were regarded by the reviewers as eutectic temperature data and included in the calculation of the mean values for these eutectic temperatures.

The data that we judged to be acceptable for the REC_2-C eutectic temperatures were averaged for each dicarbide, and the corresponding reduced temperatures calculated. These data, along with the acceptable melting point data for the dicarbides, are presented in Table 3 and plotted in Fig. 4. The plotted data show a fair correlation between the atomic number of the lanthanide in the dicarbides and the averaged values of the temperature of most of the REC_2-C eutectics. There are not enough reliable data on the melting points of the dicarbides for a responsible judgment on the acceptability of any of these data, except for LaC_2 and YC_2, whose melting points were determined by [59Spe] and [68Car], respectively, in extensive studies of the phase relationships in these systems.

Amorphous and Nonequilibrium Alloys. [78Bus] investigated magnetic and electrical properties of amorphous $Gd_{80}C_{20}$. The amorphous alloy was prepared by melt spinning in purified argon. X-ray diagrams were taken using

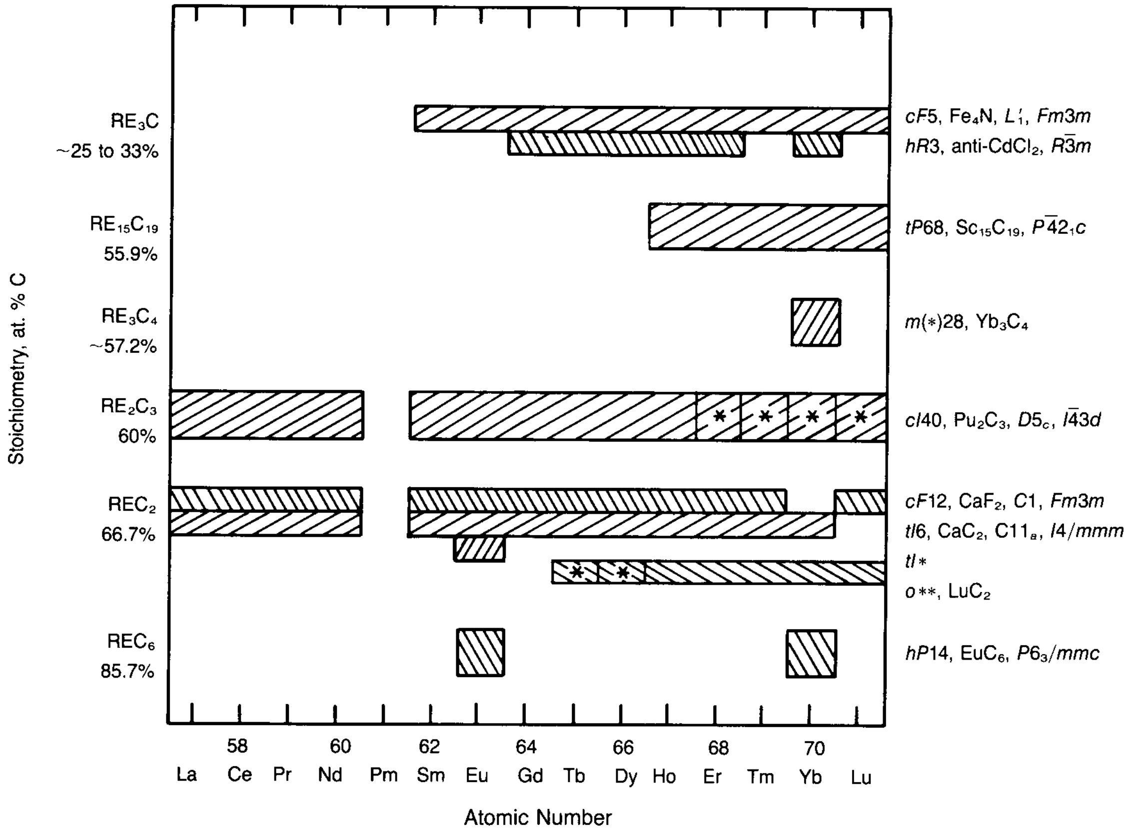
CuK_α radiation, and the scattering vector of the first amorphous peak was used to derive the distance of closest approach between Gd atoms. Of the seven different amorphous Gd-*M* (*M* = C, Al, Ni, Cu, Ga, Rh, or Pd) alloys prepared, only $Gd_{80}C_{20}$ was not ferromagnetic, and no ordering was observed down to 4.2 K.

Crystal Structures and Lattice Parameters

Compound formation in the RE-C systems is summarized in Fig. 5. Crystal structure and lattice parameter data are presented in tables accompanying each individual evaluation in this and future issues. Parameters listed in the tables are the mean values when more than one acceptable set of data was presented for a particular form. The number of references is generally indicative of the number of sets of reported lattice parameter data that were used in obtaining the average value(s). However, in some instances, the same data were presented in more than one paper. In such situations, each paper is cited, but the data are not weighted by duplicate entries. Densities were calculated using the average values for the lattice parameters, the known structures, and the standard atomic weights of the component elements. When data have been rejected, a brief explanation is appended to the table and, occasionally, explanatory comments on accepted data are included.

RE_3C and RE_2C Structures. Studies of the RE-C systems (RE = Sm through Lu and Y) have established the existence of the tri-rare-earth carbides in two related forms. All of the tri-rare-earth carbides have the cubic C-deficient NaCl-type structure, commonly known as the Fe_4N-type, L'_1. For those phases that have been shown to be polymorphic (RE = Gd, Tb, Dy, Ho, Yb, Sc, and Y), the Fe_4N-type structure is the high-temperature phase and can also exist at room temperature in a metastable state. In this form, lanthanide atoms are arranged in a cubic close-packed structure with C atoms distributed randomly over the octahedral sites. RE_3C phases exist over a wide solid solubility range. [58Spe] reported that in the Y-C system, this form exists from about $YC_{0.25}$ (Y_4C) to about $YC_{0.40}$ (Y_5C_2) and referred to this carbide as "triyttrium carbide" because Y_3C lies approximately midway between these limits.

Fig. 5 Compound Formation in the RE-C Systems



The high-temperature crystal structures (CaF_2-type, C1) for the REC_2 phases where RE = Pr, Nd, Sm, Gd, Dy, Ho, Er, and Tm have not been confirmed by X-ray methods. These structures are assumed on the basis of the reported $\alpha \rightleftarrows \beta$ transformation (see text "Solid State Transformation Temperatures of REC_2"). The compounds marked by an asterisk (*) are metastable structures formed only under high pressure. Some evidence has been reported for the existence of REC_6 where RE = Ce, Pr, Nd, and Sm (see text "REC_6 Phases").
K.A. Gschneidner, Jr. and F.W. Calderwood, 1986.

[68Car] developed the phase diagram for the Y-C system (see "The C-Y (Carbon-Yttrium) System," to be published) and observed this triyttrium carbide along with two other intermediate phases, Y_2C_3 and YC_2. They found the compositional range of this form to be temperature dependent. Their phase diagram showed the Y-rich phase boundary to have a minimum C content at ~16 at.% C ($YC_{0.19}$), and at high temperatures the monophasic region for this form extended across the diagram to the YC_2 composition. [71Sto], using a mass spectrometer, thermal analysis, and X-ray diffraction, also studied the Y-C system and observed the lower limit for C in this phase to be about 26 at.% C ($YC_{0.35}$), instead of ~16 at.% C reported by [68Car]; otherwise their investigations are in good agreement.

Although [58Spe] reported that this tri-rare-earth carbide phase exists for RE = Sm to Lu (except for Eu) and for Y, but not for RE = La through Nd, they did not attempt to establish solubility limits for all RE_3C compounds, noting only that similar limits of solubility probably exist in the other systems. [70Lap] prepared this phase with Eu. No data have been reported for a cubic Sc_3C phase, but [68Ato] and [69Kri] reported trigonal Sc_2C data (see below).

The stable room temperature form has the $CdCl_2$-type rhombohedral structure and is designated αRE_2C in the crystal structure tables in the individual evaluated RE-C systems. The composition of this form is close to RE_2C. Structure data found in the literature for the room temperature form include lattice parameters for six RE_2C compounds (RE = Gd, Tb, Dy, Ho, Yb, Sc, and Y). No lattice parameter data were found for this carbide where RE = Sm, Eu, Er, Tm, or Lu, but Er_2C was reported to crystallize in this structure [81Ato].

In the crystal structure tables for the individual RE-C phase diagrams the high-temperature cubic RE_3C phase is designated βRE_3C and the reported lattice parameters are for the C-rich composition. But for four rare-earth metals (Eu, Dy, Y, and Yb) for which information is available, the lattice parameters of the rare earth-rich compositions are also reported.

Structures of Sesquicarbides and Other Compounds Near 60 at.% C. [58Spe] showed that sesquicarbides of the light lanthanides (RE = La through Ho; Pm and Eu not examined) can be prepared in the bcc form directly by arc melting. The sesquicarbides of the heavier lanthanides and Y were found to form a low-symmetry crystal structure. Ho_2C_3 was observed to be dimorphic. [69Kru], using a high-pressure, high-temperature technique, prepared Y_2C_3 in the bcc form and suggested that the isostructural sesquicarbides could be prepared in the same manner. Subsequent investigations [70Kru, 80Nov] showed this to be correct for the RE_2C_3 phases for Er through Lu. Lattice parameters that have been reported for these metastable Pu_2C_3-type compounds are listed in the crystal structure tables for the individual RE-C systems.

[68Car] studied the Y-C system and reported monophasic microstructures in the region 55 to 58 at.% C, but they were not successful in indexing the X-ray pattern. [71Bau] determined the crystal structure for this form and found the composition to be $Y_{15}C_{19}$ (55.9 at.% C). Using single-crystal X-ray methods, [71Jed] obtained the same pseudocubic tetragonal cell for $Sc_{15}C_{19}$. [74Bau] and [80Bau] reported a similar composition and structure for Er, Yb, and Lu alloys. [70Has] studied the Yb-C system and found a monoclinic $YbC_{1.25+y}$ compound where $0 \leq y \leq 0.16$, approximately 55.5 to 58.3 at.% C.

REC_6 Phases. The existence of EuC_6 and YbC_6 was established about 10 years ago by [75Gue]. More recently [80Elm] presented evidence that they had prepared the REC_6 compounds for RE = Ce, Pr, Nd, and Sm. [80Elm] listed values for I_c, the identity period along the c axis as measured from the "001" reflections of the respective powder diagrams: 0.449 nm, 0.457 nm, 0.453 nm, and 0.47 nm. They did not report a complete structural study so it is not known if these compounds have the same structure as C_6Eu and C_6Yb. [75Gue] also prepared a C_6Sm compound with $a = 0.431 \pm 1$ nm and $c = 0.458 \pm 8$ nm.

Thermodynamics

Gaseous State

Thermodynamic studies of gaseous rare-earth dicarbides generally combine the use of a mass spectrometer and a high-temperature Knudsen effusion cell. Species present in the cell are determined as a function of temperature, a reaction is assumed or determined, and thermodynamic data are obtained for this reaction by either the second-law or the third-law method. The second-law method utilizes the Clausius-Clapeyron plot of the variation of the equilibrium constant with temperature, and the third-law method combines the Gibbs energy change of the reaction, deduced from a measured equilibrium constant, with a known or estimated entropy change. Where no spectroscopic information is available on the metallic carbides, it is necessary to assume a molecular model and to estimate the various forces, such as vibrational frequencies or bending moments, that enter into the entropy change. In many cases, third law-calculations were performed utilizing several model configurations, and then a preferred model was chosen based on the internal consistency of the thermodynamic results obtained by the various methods of evaluation.

Pertinent heat content and Gibbs energy function values for various species involved in the calculation of thermodynamic functions have been tabulated by several investigators and the sources for these reported data are shown in Table 4.

REC_n Species. Thermodynamic properties of one REC species were reported in the literature. [69Gin] studied chemical equilibria of the reaction $CeC_2(g) + Ce(g) \rightleftarrows CeC(g)$ by the mass spectrometer-Knudsen effusion cell method and found the enthalpy change for the reaction to be 125.1 ± 2.1 kJ/mol of atoms. Combining this value with the heat of atomization of CeC_2, 425.6 ± 2.1 kJ/mol of atoms (a preliminary value given by [67Bal] in a progress report, later refined to 424.7 ± 2.1 kJ/mol of atoms as listed in Table 5), he obtained a dissociation energy of the diatomic molecule, $D_0(CeC) = 150.6 \pm 9.8$ kJ/mol of atoms. [83Kin] also studied the equilibrium reaction $CeC(g) \rightleftarrows Ce(g) + C(s)$ by the Knudsen effusion-mass spectrometry method and obtained the values listed in Table 5 for the enthalpy change of the reaction, the enthalpy of formation of CeC(g) at 298 K, and the atomization energy of CeC(g) at 0 K.

The same type of equilibrium reaction $REC_n(g) \rightleftarrows RE(g) + nC(s)$ was used by several different investigators to explore thermodynamic properties of several RE-C species, and their results are listed in Table 5. For $LaC_n(g)$ species, $n = 2$ to 8; for $CeC_n(g)$, $n = 1$ to 6; and for $ScC_n(g)$ and $YC_n(g)$, $n = 2$ to 6. For the other $REC_n(g)$ species investigated, $n = 2$ only. The Knudsen effusion-mass spectrometer method was employed in all of these investigations, many of which involved K.A. Gingerich and his associates.

[71Fil1] employed the Knudsen cell-mass spectrometer method to study C_2 exchange reactions of the type $REC_2(g) + RE'(g) \rightleftarrows RE'C_2(g) + RE(g)$ where RE and RE' are different lanthanide metals. Eleven combinations were studied, and the dissociation energies of the gaseous dicarbides, shown in Table 6, were determined from the enthalpies of the reaction combined with the known dissociation energy of gaseous CeC_2 (225.9 ± 2.8 kJ/mol of atoms). Trends in the heats of formation and sublimation of the rare-earth dicarbides were used to estimate dissoci-

Table 4 Thermal Functions Reported for Various $REC_n(g)$ Species

Species	Thermal functions		Temperature range, K	Reference
	$-(G^0_T-H^0_0)/T$	$(H^0_T-H^0_0)$		
$CeC(g)$	x	x	298, 2200 to 2800	[83Kin]
$LaC_2(g)$	x	...	1600 to 2400	[68Fai]
	x	x	298, 2000 to 2500	[71Kohl]
	x	x	2100 to 2500	[71Fil2]
	x	x	298, 1800 to 2800	[71Ste]
	x	x	298, 2000 to 3200	[81Gin]
$CeC_2(g)$	x	...	1600 to 2400	[68Fai]
	x	x	298, 1800 to 2500	[69Bal2]
	x	x	2000 to 2400	[71Fil3]
	x	x	2100 to 2500	[71Fil2]
	x	x	298, 2200 to 2800	[83Kin]
$PrC_2(g)$	x	x	2100 to 2500	[71Fil2]
$NdC_2(g)$	x	...	1600 to 2400	[68Fai]
	x	...	1800 to 2300	[67Dem]
	x	x	2100 to 2500	[71Fil2, 72Fil]
$EuC_2(g)$	x	x	1800 to 2400	[72Bal]
$GdC_2(g)$	x	x	2000 to 2400	[71Fil3]
$TbC_2(g)$	x	x	2000 to 2400	[71Fil3, 72Fil]
$DyC_2(g)$	x	...	2000 to 3000	[69Bal3]
	x	x	2100 to 2500	[72Fil]
$HoC_2(g)$	x	...	2000 to 3000	[69Bal3]
	x	x	2100 to 2500	[72Fil]
$ErC_2(g)$	x	x	1800 to 2700	[69Bal4]
	x	x	2100 to 2500	[72Fil]
$TmC_2(g)$	x	x	2100 to 2500	[72Fil]
$LuC_2(g)$	x	x	298, 2000 to 2600	[72Gui]
$ScC_2(g)$	x	x	298, 2000 to 2500	[71Kohl]
	x	...	2000 to 2100	[65Ver]
	x	...	2200 to 2400	[71Koh2]
	x	x	298, 1800, 2600	[81Haq]
$YC_2(g)$	x	...	1900 to 2400	[65Dem]
	x	x	298, 1800 to 2800	[70Koh]
$LaC_3(g)$	x	x	298, 2000 to 3200	[81Gin]
$CeC_3(g)$	x	x	298, 2200, 2800	[83Kin]
$ScC_3(g)$	x	x	298, 1800, 2600	[81Haq]
$LaC_4(g)$	x	x	298, 1800 to 2800	[71Kohl]
	x	x	298, 1800, 2800	[71Ste]
	x	x	298, 1800 to 3200	[81Gin]
$CeC_4(g)$	x	x	298, 1800 to 2500	[69Bal2]
	x	x	298, 2200 to 2800	[83Kin]
$DyC_4(g)$	x	...	2000 to 3000	[69Bal3]
$HoC_4(g)$	x	...	2000 to 3000	[69Bal3]
$LuC_4(g)$	x	x	298, 2000 to 2600	[72Gui]
$ScC_4(g)$	x	x	298, 1800 to 2800	[71Kohl]
	x	x	2200 to 2400	[71Koh2]
	x	x	298, 1800 to 2600	[81Haq]
$YC_4(g)$	x	x	298, 1800 to 2800	[70Koh]
$LaC_5(g)$	x	x	298, 2000 to 3200	[81Gin]
$CeC_5(g)$	x	x	298, 2200 to 2800	[83Kin]
$ScC_5(g)$	x	x	298, 1800 to 2600	[81Haq]
$LaC_6(g)$	x	x	298, 2000 to 3200	[81Gin]
$CeC_6(g)$	x	x	298, 2200 to 2800	[83Kin]
$ScC_6(g)$	x	x	298, 1800 to 2600	[81Haq]
$LaC_7(g)$	x	x	298, 2400 to 3200	[82Gin]
$LaC_8(g)$	x	x	298, 2400 to 3200	[82Gin]

ation energies of SmC_2, EuC_2, YbC_2, and LuC_2. These estimated values are enclosed in parentheses in Table 6.

The constants A and B for the log pressure equation $\log P$ (atm) $= A/T + B$ for the vaporization of REC_2 compounds and the enthalpies of vaporization are listed in Table 7.

Some investigators reported enthalpy changes for the reaction $REC_2(g) + 2C(s) \rightleftarrows REC_4(g)$ (see Table 8), from which they calculated the atomization energies of $REC_4(g)$ (Table 5).

[58Chu] used a mass spectrometer to observe gaseous LaC_2 in equilibrium with La(g) and C (graphite), and for

Table 5 Enthalpy Change for the Reaction RE(g) + nC(s) $\rightleftarrows$ REC$_n$(g), Standard Enthalpy of Formation, and Atomization Energy of REC$_n$ species

Species	Enthalpy change (ΔH^0_0), kJ/mol	Enthalpy of formation ($\Delta_f H^0(298)$), kJ/mol	Atomization energy ($\Delta H^0_{a,0}$), kJ/mol	Reference
$CeC(g)$	136 ± 1.8	347 ± 6	220.5 ± 6	[83Kin]
$LaC_2(g)$(a)	53.1 ± 1.3	197.3 ± 2.0	421.0 ± 1.7	[81Gin]
$CeC_2(g)$	48.4 ± 1.5	...	424.7	[65Bal, 69Bal1, 69Bal2]
	51.4 ± 0.6	195.8 ± 0.9	422.7 ± 1.7	[81Gin]
$PrCe(g)$	61.4	...	411.4	[69Bal1]
$NdC_2(g)$	68.3	...	404.5	[69Bal1]
	69.2 ± 3.9	...	405.9 ± 5.6	[67Dem]
$EuC_2(g)$	94.8 ± 4.2	...	378.0 ± 5.6	[72Bal]
$GdC_2(g)$(b)	61.4	...	411.4	[69Bal1]
$DyC_2(g)$	88.8	...	384.2	[69Bal1]
	89.3 ± 2.7	...	383.8 ± 3.1	[69Bal3]
$HoC_2(g)$	90.0	...	383.1	[69Bal1, 69Bal3]
$ErC_2(g)$	87.2 ± 3.6	...	385.8	[69Bal4]
$LuC_2(g)$	71.1 ± 4.2	...	401.7 ± 5.6	[72Gui]
$ScC_2(g)$	86.7 ± 7.9	...	385.0 ± 7.0	[71Koh2]
	79.1 ± 2.8	205.5 ± 4.0	395.0 ± 4.7	[81Haq]
$YC_2(g)$	63.4 ± 5.7	...	409.7 ± 5.7	[70Koh]
	55.1 ± 1.3	...	419.0 ± 5.0	[80Gin]
$LaC_3(g)$	78.6 ± 1.3	187.0 ± 1.8	454.8 ± 1.8	[81Gin]
$CeC_3(g)$	75.2 ± 1.2	185.0 ± 2.8	458.3 ± 2.8	[83Kin]
$ScC_3(g)$	88.8 ± 4.0	183.3 ± 5.0	444.9 ± 5.8	[81Haq]
$YC_3(g)$	82.2 ± 2.2	...	451.3 ± 7.5	[80Gin]
$LaC_4(g)$	63.5 ± 1.0	150.8 ± 1.6	505.4 ± 1.4	[81Gin]
$CeC_4(g)$	...	...	509.6 ± 4.2(c)	[69Bal2]
	66.7 ± 0.6	151.8 ± 1.8	502.4 ± 1.8	[83Kin]
$NdC_4(g)$	...	...	498.7 ± 4.2(c)	[68Bal]
$DyC_4(g)$	...	...	481.9 ± 4.4(c)	[69Bal3]
$HoC_4(g)$	...	...	482.6 ± 1.9(c)	[69Bal3]
$LuC_4(g)$	...	...	490.4 ± 7.5(c)	[72Gui]
$ScC_4(g)$	88.2 ± 4.2	...	479.5 ± 4.2	[71Koh2]
	78.0 ± 0.8	154.4 ± 3.6	490.9 ± 4.4	[81Haq]
$YC_4(g)$	75.5 ± 3.5	...	492.2 ± 3.6	[70Koh]
	62.9 ± 0.8	...	506.0 ± 4.8	[80Gin]
$LaC_5(g)$	72.5 ± 7.0	145.0 ± 7.0	520.2 ± 7.5	[81Gin]
$CeC_5(g)$	74.1 ± 0.4	145.3 ± 2.5	518.5 ± 2.5	[83Kin]
$ScC_5(g)$	69.4 ± 3.3	133.0 ± 4.0	523.2	[81Haq]
$YC_5(g)$	79.1 ± 1.3	...	513.5 ± 5.8	[80Gin]
$LaC_6(g)$	71.4 ± 6.0	133.7 ± 6.0	542.1 ± 6.4	[81Gin]
$CeC_6(g)$	73.2 ± 0.4	135.1 ± 2.0	535.4 ± 2.0	[83Kin]
$ScC_6(g)$	70.08	124.9 ± 4.0	539.4 ± 4.9	[81Haq]
$YC_6(g)$	69.1	...	540.1 ± 8.5	[80Gin]
$LaC_7(g)$	82.1 ± 1.0	136.9 ± 6.3	540.0 ± 7.5	[82Gin]
$LaC_8(g)$	77.8	126.7 ± 6.7	554.3 ± 7.8	[82Gin]

Note: The entity for mol is mol of atoms.

(a) For this reaction, [58Chu] reported that for La, the enthalpy of the reaction at midrange (2400 K) is 58.6 kJ/mol, and [63Jac] reported $\Delta H^0_{2200} = 50 \pm 2$ kJ/mol. No ΔH^0_0 value was given by either group of investigators. (b) For Gd, [62Jac] reported the enthalpy of the reaction is 52.9 ± 0.7 kJ/mol at midrange (2150 K), but no ΔH^0_0 value was given. (c) These data were calculated from the reaction ΔH^0_0 for reaction $REC_2(g) + 2C(s) \rightleftarrows REC_4(g)$ (see Table 8).

Data not used: An earlier value reported by [65Bal] for $\Delta H^0_{a,0}$ of PrC_2 (418.4 ± 7.0 kJ/mol) was not used because it was superseded by a later value (411.4 kJ/mol) reported by the same group [69Bal1]. Values of $\Delta H^0_{a,0}$ reported by [65Bal] for CeC_4 and HoC_4 (508 ± 7.5 and 489.5 ± 11.7 kJ/mol, respectively) were not included because later reports [69Bal2, 69Bal3] from this group gave 509.6 ± 4.2 and 482.6 ± 1.9 kJ/mol for the same property of these species. [76Gin] reported for the enthalpy of atomization of gaseous CeC_3, CeC_5, and CeC_6 the values 450.5 ± 7.5, 512.8 ± 6.7, and 540.3 ± 5.7 kJ/mol, respectively. Because [83Kin] are the same group of investigators as [76Gin] only their more recent data were included. [81Lvo] obtained atomization energy data on gaseous DyC_2 using electrothermal atomic absorption spectrometry. They reported 423 ± 3.4 kJ/mol for their second-law determination and 426 ± 9 kJ/mol for their third-law determination of $\Delta H^0_{a,0}$. These data are ~11% larger than the value reported by [69Bal3]. Because the values of [69Bal3] are more in line with those of other REC_2 species, the reviewers did not include the data reported by [81Lvo].

Table 6 Dissociation Energies of Rare-Earth Dicarbides Obtained from the Exchange Reaction $REC_2(g) + RE'(g) \rightleftarrows RE(g) + RE'C_2(g)$ at 0 K

Phase	Dissociation enthalpy, kJ/mol of atoms
$LaC_2(g)$	223.1 ± 4.2
$CeC_2(g)$	225.9 ± 2.8
$PrC_2(g)$	210.6 ± 4.2
$NdC_2(g)$	200.8 ± 4.2
$SmC_2(g)$	161.8 ± 9.8(a)
$EuC_2(g)$	136.7 ± 11.2(a)
$GdC_2(g)$	210.6 ± 4.2
$TbC_2(g)$	209.4 ± 4.2
$DyC_2(g)$	185.5 ± 5.6
$HoC_2(g)$	186.9 ± 4.2
$ErC_2(g)$	188.3 ± 4.2
$TmC_2(g)$	166 ± 5.6
$YbC_2(g)$	125.5 ± 13.9(a)
$LuC_2(g)$	217.6 ± 16.7(a)

From [71Fil1]. (a) Dissociation energy values were estimated from trends in the heats of formation and sublimation of the REC_2 phases.

Table 7 Vapor-Pressure Constants and Enthalpy of Vaporization of Gaseous REC_2 Compounds for the Reaction $REC_2(g) \rightleftarrows RE(g) + 2C(g)$

Species	Log p(atm) = A/T + B		Temperature range, K	$(\Delta_{vap}H)$ at midrange, kJ/mol of atoms	Midrange temperature, K	Reference
	A	B				
CeC_2	−25 100 ± 720	5.49 ± 0.34	1990 to 2300	160.2 ± 4.6	2145	[69Bal2]
YC_2	−24 230 ± 850	4.44 ± 0.35	2270 to 2550	154.6 ± 5.4	2410	[70Koh]

Table 8 Enthalpy Change for the Reaction $REC_2(g) + 2C(s) \rightleftarrows REC_4(g)$

Species	Enthalpy change (ΔH^0_0), kJ/mol	Reference
$CeC_4(g)$	28.9 ± 3.3	[69Bal2]
$NdC_4(g)$	27.8 ± 3.0	[68Bal]
$DyC_4(g)$	31.1 ± 0.2	[69Bal3]
$HoC_4(g)$	32.2 ± 3.4	[69Bal3]
$LuC_4(g)$	43.3 ± 0.6	[72Gui]

Note: The entity for mol is mol of atoms.

the reaction $La(g) + 2C(s) \rightleftarrows LaC_2(g)$ they calculated the heat of reaction, ΔH^0_0, by means of both the second and the third law. Application of the third law involved the use of estimated entropy values, because no spectroscopic information was available for gaseous dicarbides. The enthalpy shown in Table 5 for their calculations is the mean of the values obtained by the second- and third-law methods.

According to [71Ste], [63Jac] examined the Langmuir vaporization of several rare-earth dicarbides using mass spectrometry and reported the enthalpy of reaction data that is included in footnote (a) of Table 5.

[68Fai] studied vaporization of several REC_2 compounds (RE = La, Ce, Nd, Sm, or Eu). Samples were prepared by direct combination of 99.8% (wt.?) pure RE-metal with spectrographic C at temperatures above 2000 °C. The less volatile metals, La and Ce, were mixed with C and heated in graphite crucibles contained in a W or Ta effusion cell that had a small orifice to allow C to degas without the release of significant amounts of metal vapor. The more volatile metals were mixed with C and sealed in Mo bombs under vacuum before heating in an Ar-filled tube furnace. Vapor pressures of the REC_2-graphite systems were obtained by effusing C-rich REC_2 samples from metal cells below 1600 °C or from graphite-lined metal cells at temperatures up to 2100 °C. Pressures were reproducible to ±10%. [68Fai] found significant amounts of $REC_2(g)$ and $REC_4(g)$ to be present in equilibrium with the solid dicarbides at high temperatures.

[67Win] investigated sublimation of CeC_2 over the range 1635 to 2036 °C, using the mass spectrometer-Knudsen cell method, and found the principal gaseous species in equilibrium with $CeC_2(s)$ to be $CeC_2(g)$. [69Bal2] used the mass spectrometer-Knudsen cell technique to study thermodynamic equilibrium in the Ce-C system and observed gaseous CeC_2 and CeC_4 molecules in the range 1717 to 2027 °C. [67Dem] used the same technique to study thermodynamic equilibrium in the Nd-C system over the range 1677 to 1887 °C, and having observed the gaseous molecule NdC_2, they evaluated its dissociation energy by both second- and third-law methods. [70Kys] prepared SmC_2 and EuC_2 samples by C reduction of the corresponding sesquioxides and used the mass spectrometer-effusion cell method to study thermal decomposition of these dicarbides.

[71Sei] noted discrepancies in previously reported vaporization data for SmC_2 and, taking steps to avoid hydrolysis of their specimens by atmospheric water vapor, used the target collection-Knudsen effusion technique to study decomposition pressures of both SmC_2 and TmC_2. [69Sto] used the Knudsen effusion technique to determine vapor pressure of SmC_2 in equilibrium with C (graphite) and determined weight loss from the cells by an automatic recording balance. [67Hoe] used similar means to study vaporization of GdC_2.

The investigations of [67Ave] on the Sm-C system, [67Cut] on SmC_2 and EuC_2, [69Bal3] on the Dy-C and Ho-C systems, [69Bal4] on the Er-C system, [70Koh] on the YC_2-C system, and [71Koh2] on ScC_2 utilized the mass spectroscopic-Knudsen cell technique. [66Geb2], who investigated EuC_2, utilized both the mass spectroscopic and target collection techniques.

The tetracarbide molecule, REC_4, was identified by [65Bal] during the course of a mass spectrometric study

Table 9 Vapor-Pressure Constants and Enthalpy of Vaporization of Gaseous REC_4 Species for the Reaction $2REC_2(s) \rightleftarrows REC_4(g) + RE(g)$

Species	Log p(atm) = $A/T + B$ A	 B	Temperature range, K	$(\Delta_{vap}H)$ at midrange kJ/mol	Midrange temperature, K	Reference
CeC_4	−38 800 ± 5 000	9.6 ± 2.2	2 200 to 2 300	148.5 ± 23.0	2 250	[69Bal2]
YC_4	−24 230 ± 850	4.44 ± 0.35	2 270 to 2 550	170.6 ± 3.3	2 410	[70Koh]

Note: The entity for mol is mol of atoms.

Table 10 Enthalpy Change for the Reaction $2RE(g) + nC(s) \rightleftarrows RE_2C_n(g)$, Standard Enthalpy of Formation, and Atomization Energy of Gaseous RE_2C_n Compounds

Species	Enthalpy change (ΔH_0^0), kJ/mol	Enthalpy of formation $(\Delta_f H^0(298))$, kJ/mol	Atomization energy $(\Delta H_{a,0}^0)$, kJ/mol	Reference
$Ce_2C(g)$	−112.0 ± 1.3	168.7 ± 8.7	349.0 ± 8.7	[84Kin)
$La_2C_2(g)$	−61.8 ± 10	155.3 ± 10.0	417.5 ± 10.0	[84Pel]
$Ce_2C_2(g)$	−67.0 ± 1.8	144.0 ± 6.3	422.5	[84Kin]
$La_2C_3(g)$	−41.0 ± 5.4	131.6 ± 5.4	467.8 ± 5.4	[84Pel]
$Ce_2C_3(g)$	−39.6 ± 0.2	129.4 ± 5.6	466.4 ± 5.6	[84Kin]
$La_2C_4(g)$	−35.8 ± 3.5	108.0 ± 3.5	510.0 ± 3.5	[84Pel]
$Ce_2C_4(g)$	−38.5 ± 1.4	102.5 ± 4.2	512.7 ± 4.2	[84Kin]
$La_2C_5(g)$	−21.0 ± 7.1	107.4 ± 7.1	529.0 ± 7.1	[84Pel]
$Ce_2C_5(g)$	−14.0 ± 1.3	107.1 ± 4.6	522.0 ± 4.6	[84Kin]
$La_2C_6(g)$	−16.0 ± 6.3	92.1 ± 6.3	549.4 ± 6.3	[84Pel]
$Ce_2C_6(g)$	−9.9 ± 0.5	96.3 ± 4.5	543.4 ± 4.5	[84Kin]
$La_2C_8(g)$	+3.1 ± 6.0	89.8 ± 6.0	565.8 ± 6.0	[84Pel]

Note: The entity for mol is mol of atoms.

of some RE-C systems at high temperatures. CeC_4 and HoC_4 molecules were unambiguously identified, and PrC_4 was identified tentatively by these investigators. [68Bal], [69Bal2], and [69Bal3] also reported NdC_4 and DyC_4, and [72Gui] (the same group of investigators) reported LuC_4. [70Koh] and [71Koh2] observed ScC_4 and YC_4.

Table 9 lists the constants, A and B, for the vapor-pressure equation for the reaction $2\ REC_2(s) \rightleftarrows REC_4(g) + RE(g)$ for RE = Ce and Y, the temperature range over which the relationship is valid, and the heat of vaporization calculated at mid-range. Changes in enthalpy of this reaction and the atomization enthalpy for REC_4 (RE = La, Ce, Nd, Dy, Ho, Lu, Sc, or Y) are listed in Table 5.

RE_2C_n Species. [65Wak] determined decomposition pressures for some of the carbides of Ho and reported that the sesquicarbide, Ho_2C_3, loses Ho to form the dicarbide, according to the reaction $2\ Ho_2C_3(s) \rightleftarrows 3\ HoC_2(s) + Ho(g)$.

[67Ave] measured vapor pressure of compositions in the Sm-C system by Knudsen effusion-mass spectrometer and found evidence for a stable SmC_{2-x} phase, which they stated could be Sm_2C_3, and gave an equation for the vapor pressure of the phase as a function of reciprocal temperature.

[84Kin] and [84Pel] determined thermodynamic properties of gaseous RE_2C_n species where RE = La or Ce and n = 2 to 8 for La and 1 to 8 for Ce. The change of enthalpy, ΔH_0^0, for the reaction $2RE(g) + nC(s) \rightleftarrows RE_2C_n(g)$ is listed in Table 10, along with standard enthalpies of formation, $\Delta_f H^0$(298 K), and the atomization energy, $\Delta H_{a,0}^0$, for each species. The experimental methods are similar to those employed by [81Gin], [83Kin], [81Haq], and [80Gin] for the REC_n species (see "REC_n Species" section, above).

Solid State

Heat of Formation. Investigators have utilized emf measurements at high temperatures, bomb calorimetry, and vaporization studies to determine thermodynamic properties of solid rare-earth carbides. Much of the data in the literature was obtained through vaporization studies, and it has often been necessary to use estimated thermal functions when reducing equilibrium measurements taken at an elevated temperature to 298 K. Tables of Gibbs energy functions and heat-content data were included in the reports of several investigators, and the sources of this information are listed in Table 11. Most of these data are for the dicarbides, but [82Has] listed Gibbs energy functions and heat-content data for a Pu_2C_3-type SmC_y compound (y = 1.36 to 1.45).

Enthalpy, entropy, and Gibbs energies of formation at 298 K for several REC_2 phases and a few RE_2C_3 phases are listed in Table 12. Where more than one set of these data has been reported for any compound, the reported enthalpy values for the compound were averaged. The entropy of formation values shown for the dicarbides were calculated using the known value of 23.43 J/mol · K for CaC_2 and assuming the validity of the relationship $S(REC_2) = S(CaC_2) + S(RE) - S(Ca)$.

Values for S(RE) and S(Ca) were taken from [Hultgren, E] for all RE metals and Ca except Eu, which was taken from [67Ger]. A similar calculation was performed to obtain $S(RE_2C_3)$, based on a value of 15.82 J/mol · K for Ho_2C_3 from [65Wak]. An error in the original work was corrected to obtain that value. Calculations for $S(RE_2C_3)$

Table 11 Thermal Functions for Solid Rare-Earth Carbides

Species	Thermal functions		Temperature range, K	Reference
	$-(G^0_T - H^0_0)/T$	$(H^0_T - H^0_0)$		
$SmC_{1.43}$(s)	x	x	1400 to 2000	[82Has]
LaC_2(s)	x	···	1200 to 2400	[68Fai]
CeC_2(s)	x	···	1200 to 2400	[68Fai]
NdC_2(s)	x	···	1200 to 2400	[68Fai]
SmC_2(s)	x	···	1200 to 2000	[68Fai]
	x	···	1000 to 3000	[69Sto]
	x	x	1400 to 2000	[82Has]
EuC_2(s)	x	···	1100 to 1300	[66Geb2]
	x	···	1200 to 2000	[68Fai]
GdC_2(s)	x	···	1000 to 3000	[67Hoe]
YC_2(s)	x	···	1900 to 2400	[65Dem]
	x	···	1800 to 2800	[70Koh]

Table 12 Enthalpy, Entropy, and Gibbs Energy of Formation of Solid REC_2 and Some Solid RE_2C_3 Phases at 298 K

Species	Enthalpy of formation $(-\Delta_f H^0(298))$, kJ/mol	Gibbs energy of formation $(-\Delta_f G(298))$, kJ/mol	Entropy of formation $(\Delta_f S(298))$(a), J/mol · K	Reference
LaC_2(b)	28.4	32.76	14.64	[68Fai, 71Ste, 72And, 77Mal]
CeC_2	29.0	38.77	32.77	[67Win, 68Fai, 72And, 71Bak]
PrC_2	28.2	38.41	34.27	[72And]
NdC_2(b)	28.0	37.93	33.32	[72And]
SmC_2(b)	25.4	35.23	32.97	[67Cut, 68Fai, 69Kys, 69Sto, 70Sei, 82Has]
EuC_2	22.4	33.0	35.56	[67Cut, 68Fai]
GdC_2	35.2	44.82	32.27	[72And, 73Hub]
DyC_2	31.4	41.71	34.59	[72And]
HoC_2	28.5	38.82	34.63	[65Wak, 69Bal3]
ErC_2	28.1	38.24	34.02	[69Bal4, 72And, 77Mal]
TmC_2	32.9	43.12	34.29	[71Sei]
YbC_2	25.1	33.91	29.57	[68Has]
LuC_2	39.1	47.03	26.61	[72Gui]
YC_2	34.4	41.68	24.43	[65Dem, 70Koh, 71Ste, 71Sto, 72And]
La_2C_3	38.63	36.23(c)	−8.06	[70And]
Ce_2C_3	35.33	37.24(c)	13.59	[71Bak, 70And]
Pr_2C_3	27.97	32.55(c)	15.38	[70And]
Nd_2C_3	34.09	38.33(c)	14.24	[70And]
Sm_2C_3(b)	37.0(d)	41.06	13.61	[82Has]
Ho_2C_3	11.6	16.31	15.8	[65Wak]

Note: The entity for mol is mol of atoms.

(a) Entropies of formation for the RE-dicarbides were estimated by the reviewers from $\Delta_f S(298)$ for CaC_2 = 23.43 J/mol · K and assuming $S(REC_2) = S(CaC_2) + S(RE) - S(Ca)$. Values for S(RE) and S(Ca) were taken from [Hultgren, E] except for that of S(Eu), which was taken from [67Ger]. Entropy of formation values for the RE_2C_3 phases were estimated by the reviewers using the corrected value of $\Delta_f S(298)$ from [65Wak] for Ho_2C_3 (15.82 J/mol · K) and assuming $S(RE_2C_3) = S(Ho_2C_3) + 2S(RE) - 2S(Ho)$. The values for S(RE) were taken from [Hultgren, E]. **(b)** Various authors reported only high-temperature $\Delta_{vap}H$ values for the REC_2 phases. These include: for LaC_2, $\Delta_{vap}H(T)$ = 181.3 kJ/mol at 2200 K for the reaction $LaC_2(s) \rightleftarrows La(g) + 2C(s)$ [63Jac]; for NdC_2, $\Delta_{vap}H(T)$ = 49.7 ± 4.6 kJ/mol at 2145 K for $NdC_2(s) \rightleftarrows Nd(g) + 2C(s)$ [67Dem]; for SmC_2, $\Delta_{vap}H(T)$ = 90.9 ± 5.6 kJ/mol at 1690 K for a similar reaction [67Ave]; for GdC_2, $\Delta_{vap}H(T)$ = 198.9 ± 0.8 kJ/mol at 2150 K for the reaction $GdC_2(s) \rightleftarrows GdC_2(g)$ [62Jac]. For the reaction $Sm_2C_3(s) \rightleftarrows 2Sm(g) + 3C(s)$, $\Delta_{vap}H(T)$ = 101.8 ± 6.7 kJ/mol at 1607 K [67Ave]. **(c)** [70And] reported high-temperature emf data for the sesquicarbides of La, Ce, Pr, and Nd. Utilizing fef estimates, the reviewers calculated $\Delta_f G^0(298)$ values from the $\Delta_f G^0(T)$ equations presented by the authors. **(d)** For the composition $SmC_{1.43}$.

Data not used: Some reported data for enthalpy of formation are not included in this table because of their wide divergence from the average value for the involved phases. These rejected values include: for CeC_2, −44.6 kJ/mol reported by [55Kri] and −20.9 ± 7.0 kJ/mol reported by [69Bal2]; for NdC_2, −17.4 ± 3.5 kJ/mol reported by [68Fai] and −51.2 kJ/mol reported by [73Ant]; for $EuC_{1.87}$, −13.3 kJ/mol reported by [66Geb1] and [66Geb2]; for GdC_2, −41.8 kJ/mol reported by [67Hoe]; and for DyC_2, −15.3 kJ/mol reported by [69Bal3].

were based on the relationship $S(RE_2C_3) = S(Ho_2C_3) + 2S(RE) - 2S(Ho)$. Values for S(RE) and S(Ho) were taken from [Hultgren, E].

Most of the data presented in Table 12 were obtained by the mass spectrometer-Knudsen effusion method. However, the data reported by [70And] and [72And] were obtained through a study of the dicarbide-carbon two-phase region of RE-C systems, using a solid-state galvanic cell with a calcium fluoride electrolyte. Reduction of their data by the second law gave erroneous results, but reduction of their data for LaC_2, CeC_2, and YC_2 by the third law gave values that compared favorably with literature values obtained by mass spectrometry. Their third-law data for PrC_2, NdC_2, GdC_2, DyC_2, and ErC_2 showed a systematic trend with decreasing size of the lanthanide metal. Other data in Table 12 not obtained by the mass spectrometer-Knudsen effusion method are those of [71Bak], who employed bomb calorimetry to measure $\Delta_f H(298)$ of CeC_2 and Ce_2C_3.

The enthalpy and Gibbs energy values for Ho_2C_3 appear to be anomalously low compared with those of the other sesquicarbides. In addition to the experimental thermodynamic values which have been averaged and presented in Table 12, [81Nie] calculated enthalpies of formation at 0 K according to a semiempirical model proposed by [80Mie]. These authors presented a plot of calculated versus experimental $\Delta_f H^0$ data, but they did not identify the individual dicarbides in their plot. They stated that the dicarbides of Eu and Yb (both with CaC_2 structure) are in fair agreement and that a discrepancy for the trivalent rare-earth dicarbides may be due to "the troublesome reduction of high-temperature vapor-pressure data to $\Delta_f H$ at room temperature." They presented as a table the calculated enthalpies of formation of solid borides, carbides, nitrides, silicides, and phosphides of transition and noble metals at three concentrations. Their predicted heats of formation for the carbides of La, Sc, and Y, the only RE metals included, are shown in Table 13.

Comparison of the predicted heats of formation for the dicarbides of La and Y with the experimental values shown for these compounds in Table 12 shows these predicted values to be ~100% off.

Heat Capacity Data. Debye temperatures and electronic specific heat constants for some rare-earth carbides are listed in Table 14.

Effect of Pressure

High-pressure, high-temperature methods have been used in the solid-state synthesis of several heavy lanthanide carbides. As mentioned above ("Structures of Sesquicarbides and Other Compounds Near 60 at.%"), [58Spe] found that the lighter rare-earth metals (RE = La through Ho) form a Pu_2C_3-type cubic sesquicarbide when arc melted, whereas the heavier rare-earth metals (RE = Er through Lu plus Y) form a compound of lower than cubic symmetry. Ho forms a compound with either symmetry. [71Bau] indexed the lower symmetry structure and reported it to be isotypic with tetragonal $Sc_{15}C_{19}$.

Table 13 Predicted Enthalpy of Formation of Carbides of La, Sc, and Y at Three Concentrations

Rare earth element	Predicted Enthalpy of formation ($-\Delta_f H$), kJ/mol of atoms RE_2C	REC	REC_2
La	33	50	60
Sc	44	66	70
Y	37	56	64

Table 14 Debye Temperatures and Electronic Specific Heat Constants of Some REC_x Compounds

Compound	Debye temperature, K	Electronic specific heat constant, mJ/mol · K^2	Reference
Determined by X-ray method			
$YC_{0.28}$(a)	230 ± 10	...	[68Ato]
$YC_{0.48}$(a)	170 ± 5	...	[68Ato]
Y_2C(b)	233 ± 6	...	[68Ato]
Determined by low-heat-capacity measurement			
$LaC_{1.35}$	318 ± 3	2.04 ± 0.04	[84Cor]
$YC_{1.35}$	557 ± 10	1.19 ± 0.1	[84Cor]
La_2C_3	300(c)	1.22 ± 0.26	[76Fra]
Calculated from melting point			
La_2C_3	189	...	[69Pad1]
Ce_2C_3	199	...	[69Pad1]
Nd_2C_3	203	...	[69Pad1]
LaC_2	316	...	[69Pad2]
CeC_2	310	...	[69Pad2]
PrC_2	298	...	[69Pad2]
NdC_2	311	...	[69Pad2]
GdC_2	337	...	[69Pad2]
TbC_2	292	...	[69Pad2]
DyC_2	304	...	[69Pad2]
ErC_2	308	...	[69Pad2]
TmC_2	296	...	[69Pad2]
YC_2	381	...	[69Pad2]

Note: The entity for mol is mol of atoms.

(a) Cubic. (b) Rhombohedral. (c) Estimated.

[69Kru] succeeded in preparing bcc Y_2C_3 with the Pu_2C_3-type structure by high-pressure, high-temperature methods. Starting with Y of >99.6% (wt.?) purity and spectroscopic grade C (graphite) (<50 ppm impurities), alloy samples with ~38 to ~66 at.% C were arc melted, turned, and remelted several times to insure homogeneity. Powder X-ray patterns showed the presence of Y_2C in the Y-rich samples, YC_2 in the C-rich samples, and the low-symmetry form in the samples of intermediate composition. Pressing at 15 to 25 kbar at 1200 to 1500 °C for 2 to 6 min produced bcc Y_2C_3 with the Pu_2C_3-type structure in all samples except those closest to Y_2C and YC_2 compositions. In the latter, a new low-symmetry phase was produced by the treatment. Highest yields of cubic Y_2C_3 were obtained from samples in the composition range $YC_{1.27}$ to $YC_{1.48}$ (55.9 to 59.7 at.% C). [79Ver] reported preparation of Pu_2C_3-type Y_2C_3 under pressures of 30 to 90 kbar at 1100 to 1700 °C. [70Kru] applied this technique to other heavy lanthanide carbides and succeeded in preparing cubic Pu_2C_3-type Er_2C_3, Tm_2C_3, and Yb_2C_3, but not Lu_2C_3 and Sc_2C_3. [78Ver] and [80Nov] reported synthesis of cubic Lu_2C_3 prepared under 40 to 90 Kbar at 1100 to 1500 °C. [69Kru] pointed out that high-temperature annealing of the synthesized RE_2C_3 compounds at ambient pressure destroyed the Pu_2C_3-type structure. [83Zha] also reported high-pressure synthesis of Y_2C_3.

After [67Kri] discovered that the low-temperature form of LuC_2 does not have the CaC_2-type symmetry that is found in the other rare-earth dicarbides, they attempted preparation of other REC_2 compounds in the low-symmetry crystal structure. Tetragonal forms of REC_2 (RE = Dy to Yb) were annealed at temperatures ranging from 900 to 1250 °C for time periods of 100 to 270 h (see [68Kru]). Low-order-symmetry phases isostructural with LuC_2 were observed for the materials other than DyC_2. For HoC_2 and ErC_2, [68Kru] reported transformation from the tetragonal to the low-symmetry form to occur at 1155 ± 10 and 1305 ± 10 °C, respectively. Failure to convert DyC_2 by annealing methods led to the employment of high-pressure, high-temperature techniques on these dicarbides. Tests on HoC_2 and ErC_2 produced rapid conversion and high yields of the low-order form. Tetragonal DyC_2, TbC_2, TbC_2, and YC_2 were subsequently converted by the pressure-temperature technique.

The authors observed that progressing from the heavier to the lighter lanthanide dicarbides, higher pressures, longer time periods, and lower temperatures are required. The new phases are stable at ambient pressure and temperature but require storage in an inert atmosphere. The color is metallic black, in contrast to the gold color of the tetragonal phases. Efforts to index the complex X-ray patterns yielded a structure with orthorhombic symmetry and a large unit cell volume. There was no systematic change in the lattice parameters with change in the lanthanide metal.

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